Synthesis and evaluation of acetylenic polymers as precursors for carbon fibres.

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SUMMARY

It was the aim of this work to develop a concept for a new precursor for carbon fibres. Carbon fibres, mainly on account of their low densities, high strengths and high moduli, find use as reinforcing materials in composites. They are still relatively expensive materials and their use in composites, in preference to cheaper materials like glass fibres, is justified by the properties that they impart to the composite.

Poly(acrylonitrile) [PAN] and pitches, predominantly graphitizing pitches which display liquid crystalline behaviour [mesophase pitches], are the most widely used precursors for the preparation of carbon fibres today. The mechanical properties of the carbon fibres obtained from these precursors are excellent, but the processes for their conversion into the end product pose certain problems. The effective manufacture of carbon fibres from PAN requires an oxidizing treatment which takes several hours. The polar nature of the polymer results in strong intramolecular attractive forces which impede the diffusion of the oxidizing gas, like air, into the fibre. In addition to this, the presence of nitrogen in the polymer reduces the yield of carbon obtained from it. The process in the case of mesophase pitch suffers from handling problems. The precursor fibre is extremely brittle due to its high aromatic content, and the utmost care needs to be taken during its carbonization. In addition to this, the formation of mesophase takes place at high temperatures, which results in extensive gas formation during the process. This leads to problems during the spinning of fibres from this material.

A study of the various polymeric precursors suggests that the ability of ring formation or ring coalescence during carbonization is important. This is because the source of the mechanical properties of carbon fibres is graphitic layers which are oriented along the fibre axis during heat treatment. Taking this into consideration, we decided on the use of poly(vinylacetylene) [PVA] as an alternative precursor. This polymer consists of a saturated all-carbon backbone and pendent acetylenic groups, and structurally resembles PAN. It has a higher carbon content than PAN, and the same ability to cyclize into a ladder polymer. Its highly active acetylenic groups were expected to speed up the process for the conversion into carbon fibres. Additional advantages would be a higher carbon yield, no release of volatiles during cyclization, the better oxygen permeability of the apolar polymer, and fewer handling problems as compared to the case of mesophase pitch. The thesis begins with a brief chapter on carbon fibres, including the concept, their properties, their applications, and our concept

for the new precursor. The second chapter is a literature review on the synthesis of PVA. We could conclude that the polymer cannot be synthesized directly from monovinylacetylene. A published synthetic route involved protection of the acetylenic group in monovinylacetylene with a trimethylsilyl group, in order to selectively polymerize the vinyl group. Hence, the anionic or radical polymerization of trimethylsilyvinylacetylene [TMSVA] yielded PVA after hydrolytic cleavage of the protective group. The anionic polymerization was claimed to be of the "living" type, which led us into believing that we could use this route to synthesize high molecular weight PVA. Chapter 3 describes why we were unable to synthesize high molecular weight polymers by anionic or thermally initiated radical polymerization. This chapter also reports the surprising discovery that TMSVA undergoes a slow, self-initiated polymerization to give an ultra high molecular weight polymer when stored at low temperatures. Why this approach of using the trimethylsilyl protective group to synthesize PVA is unfeasible, is also elaborated in this chapter.

In the next approach, chapter 4, we attempted to modify PVC by the nucleophilic substitution of its side groups in order to obtain PVA. PVC is an easily available polymer, and it would have been viable to synthesize PVA through a one-step reaction. However, we were unsuccessful in our attempts because dehydrochlorination seems to be the predominant reaction taking place when PVC is reacted with acetylide ions. This led us into suggesting another polymer that could be dehydrochlorinated in order to prepare PVA.

Chapter 5 describes another route to PVA, or what we called the "titration" polymerization of monovinylacetylene [VA]. In this method, VA was reacted with butyllithium [BuLi] to form lithiumvinylacetylide. The addition of a slight excess of the BuLi resulted in its selective polymerization through the vinyl group. The VA was titrated against its lithiating agent by using the coloured charge transfer complex formed between the agent and the solvent THF as an indicator of the point of equivalence; hence the name. Reprotonation of the acetylenic group yielded PVA. Reasonable molecular weights were obtained through this one-pot synthesis, and we were able to make fibres from the polymer through melt-spinning.

Chapter 6 covers a preliminary evaluation of the polymer as a carbon fibre precursor. Thermogravimetric analysis is a useful tool for this purpose. The yield of carbon obtained

on heating a sample of the polymer up to 900°C, and the shape of the curve obtained, helps us to study its decomposition behaviour. The yield was improved drastically by subjecting the fibres to an oxidative treatment in air. The period of this treatment was optimized. Furthermore, a possible structure that develops during oxidation is proposed.

Taking into consideration the problems associated with the synthesis of large quatities of processable PVA, and the need for an oxidation step for its conversion into carbon fibres, an entirely new strategy was thought of. The concept involved the polymerization of 3-butyn-2-one to obtain a polyacetylene with pendent methyl ketonic groups. These groups could be cyclized through thermal treatment to give a ladder polymer with two parallel, conjugated chains, i.e. polyacene. There would be no need for protective groups to carry out the polymerization, or the oxidation step to bring about dehydrogenation of the ladder polymer obtained. The final chapter is about some preliminary work that was carried out to synthesize poly(3-butyn-2-one). Another possible route to synthesize the polymer has been evaluated, and other alternative precursors for carbon fibres have been put forward, which could serve as guidelines for future work in this direction.